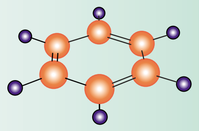
Theoretical Calculations of Electron Affinities and Correlation with Experiment

L.D. Betowski[1], M.A. Enlow[1], L. Riddick[1], D.H. Aue[2] and M. Guidoni[2]

1. U.S. Environmental Protection Agency, NERL, P.O. Box 93478, Las Vegas, NV 89193
2. Department of Chemistry, University of California, Santa Barbara, CA 93106

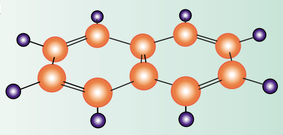
1 INTRODUCTION

Quantum chemistry is capable of calculating a wide range of electronic and thermodynamic properties of interest to a chemist or physicist. Calculations can be used both to predict the results of future experiments and to aid in the interpretation of existing results. Quantum chemistry can also be applied to biological processes such as toxicity and carcinogenicity. Here we will present examples of how quantum chemistry can be used to: (1) examine the influence of electron affinities on the sensitivity of compounds under negative ion chemical ionization conditions; and (2) investigate the biological activity of a class of environmentally significant organic compounds, polycyclic aromatic hydrocarbons (PAHs).



2 METHODS

The simplest method for the calculation of vertical electron affinities consists of performing a geometry optimization on the neutral form of the species of interest and using the LUMO energy (Koopmans' approximation). Although the Koopmans' approximation often provides reasonable estimates of ionization energies due to a fortuitous cancellation of errors, it usually fails to provide a reasonable estimate of electron affinities. A more advanced method involves performing a second calculation on the anionic form of the species of interest at the geometry of the neutral form. The vertical electron affinity can then be determined either by taking the difference in total energies between the neutral and anion or more simply by using the HOMO energy of the anionic form (which formally is equal to the vertical ionization energy of the anion). Finally, a number of propagator methods such as the Outer Valence Greens Functional method (OVGF) exist. These have the advantage of being a single calculation rather than taking the difference in energy between two calculations and they formally include electron correlation and electron relaxation effects.



All calculations were performed using the Gaussian 94 program suite. Complete geometry optimizations for the neutral forms of all molecules were first carried out at the HF/6-31G(d) level of theory followed by frequency calculations in order to verify that the stationary points thus obtained were true minima. Geometries were then further optimized at the HF/6-311G(d,p) level of theory. Single point calculations were then performed on the anionic species at the HF/6-311G(d,p) level of theory using the optimized geometry of the neutral. Calculations on the open shell ions were performed using the spin unrestricted formalism. Vertical electron affinities of the neutral species were obtained from the Koopmans' approximation to the first ionization energy of the anion at the geometry of the neutral. The geometry of the anion was then optimized at the HF/6-311G(d,p) level of theory. The difference in energy between the anion at its optimized geometry and at the geometry of the neutral form of the molecule is its relaxation energy. This relaxation energy was added to the vertical electron affinity to obtain the adiabatic electron affinity.

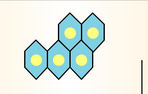
3

Vertical and Adiabatic Electron Affinities (EA) for Azulene calculated by a variety of methods and basis sets. All data in eV.

	HF/6-311G(d,p)	HF/6-311++G(d,p)
Vertical EA Methods		
Koopmans, Neutral LUMO	-1.330	-0.993
OVGF	-0.628	-0.748
DE	-0.160	0.040
Koopmans, Anion[a] HOMO	0.384	0.584
Adiabatic[b] EA Methods		
DE	0.097	0.290
Anion[a] HOMO + Relaxation Energy	0.642	0.834

(a) The anion at the optimized geometry of the neutral species.
(b) The experimental adiabatic EA for Azulene is 0.694 +/- 0.100 eV, Chowdhury, S.; Henis, T.; Grimsrud, E.P.; Kebarle, P.; *J. Phys. Chem.*, 1986, 90, 2747.

4



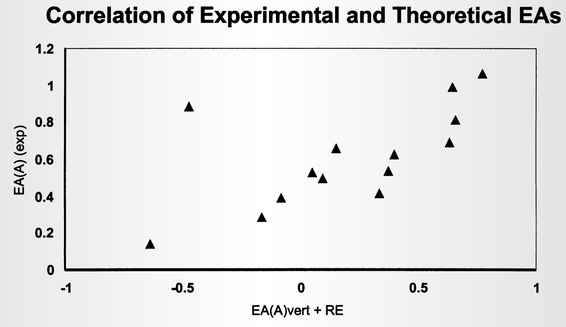
	Benzo(a)pyrene	Benzo(e)pyrene
Carcinogenicity	Very high	None
Log (N/P) Sensitivity[1]	+2.60	-0.33
EA (calculated)	0.668	0.054
EA (experimental)	0.815	0.534

1. Daishima, S.; Iida, Y.; Shibata, A.; Kanda, F. *Org. Mass Spectrom.* 1992, 27, 571-577.

As this table shows, for the two isomers, benzo(a)pyrene and benzo(e)pyrene, the extreme difference in carcinogenicity is reflected in both the difference in the ratio of negative to positive ion sensitivity and in the calculated EAs.

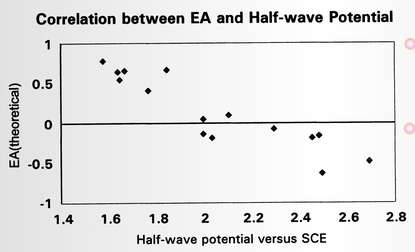
5

The correlation of experimental adiabatic electron affinities and theoretical electron affinities calculated via Koopmans' Theorem and relaxation energy correction.



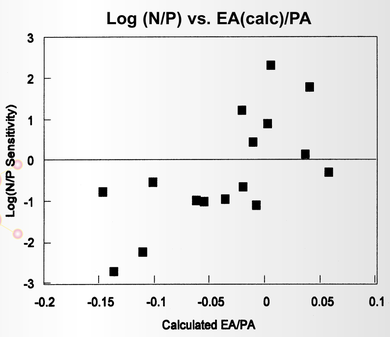
6

The correlation between the calculated electron affinity and the half-wave potential ($-e_{1/2}$) versus SCE.



7

The correlation of the log of the ratio of the negative to positive ion sensitivity with the ratio of the calculated electron affinity to the proton affinity.



8 CONCLUSIONS

Calculation of electron affinities has traditionally been a difficult operation. EAs involve odd-electron systems. Spin contamination becomes a problem, and diffuse functions, which are useful in describing the overall wave function for a system that has an extra electron, add complexity to the calculations. Consequently, most of the research involving the calculation of this property has involved systems with small numbers of electrons. In order to deal with larger systems, correlation of calculated EAs with the experimental values becomes imperative. Four different methods of calculating EAs were used, and, within the constraints of basis sets and level of theory, the Koopmans' Theorem approximation on the anion came closest to both predicting the experimental values and correlating to the experimental data. These correlations are useful both in predicting EAs for those compounds with no experimental values and in identifying outliers in the experimental data. The use of EA to predict negative ion sensitivity under chemical ionization mass spectrometric conditions has proved to be fairly successful. The calculated EA for benzo(e)pyrene reflects the insensitivity of negative ion CI for the compound better than the experimental EA.